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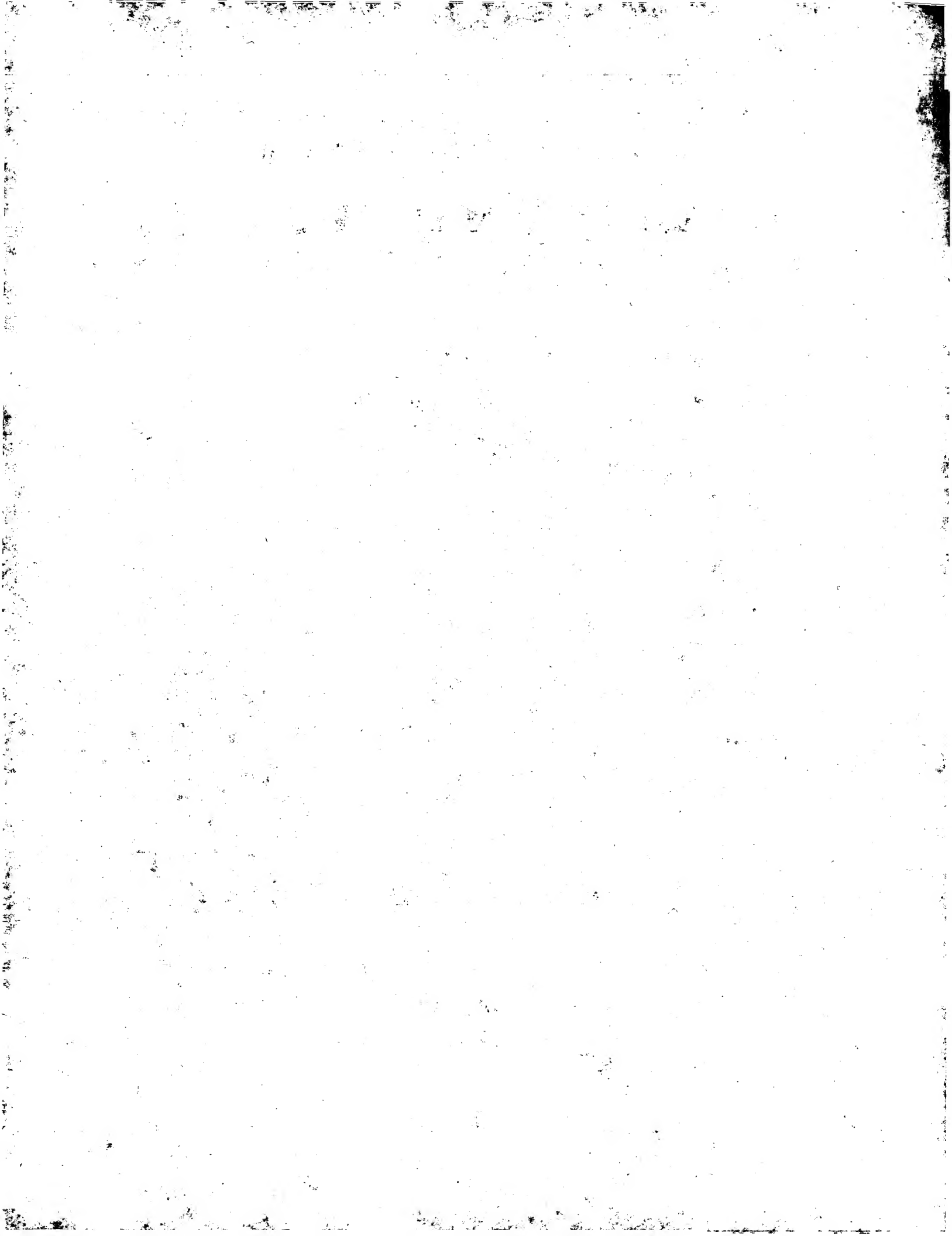
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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Edgar E. Steenwinkel, et al.

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For: Preparation Of Iron Compounds
By Hydrothermal Conversion

Commissioner for Patents
P.O. Box 1450
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CERTIFICATE OF MAILING

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Sir:

Enclosed herewith is a certified copy of European Patent Application Serial No 02078407.0, filed on August 16, 2002.

Respectfully submitted,

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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R C van Dijk



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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
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Preparation of iron compounds by hydrothermal conversion

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PREPARATION OF IRON COMPOUNDS BY HYDROTHERMAL CONVERSION

The present invention relates to a process for the hydrothermal conversion of a starting iron compound selected from the group consisting of iron oxides, iron hydroxides, iron oxyhydroxides, and mixtures thereof into a product iron compound, the product iron compound having different physical, chemical, and/or structural properties than the starting iron compound.

It is known from the prior art to convert goethite ($\alpha\text{-FeOOH}$) into hematite ($\alpha\text{-Fe}_2\text{O}_3$) in a suspension under hydrothermal conditions. RO 86979 discloses this conversion using an autoclave and temperatures of about 210°C . The same conversion, but now in the presence potassium carbonate using temperatures between 180 and 210°C and pressures between 16 and 20 atm., is disclosed in RO 100113.

In order to minimise the costs of operation and to maximise energy conservation, it would be desirable to conduct the hydrothermal conversion of iron oxides, iron hydroxides, and iron oxyhydroxides in a continuous mode.

However, as will explained below, processes involving suspensions are not easy to conduct continuously, mainly due to segregation and sedimentation.

Suspensions consist of a continuous phase, i.e. a liquid, and a dispersed phase, i.e. solid particles. Suspensions can be homogeneous or heterogeneous. In this specification, homogeneous suspensions are defined as suspensions having a constant volume fraction of the continuous phase throughout the whole system. Suspensions without such a constant volume fraction of the continuous phase are referred to as heterogeneous. In these heterogeneous systems there are concentration gradients of the dispersed phase.

Suspensions can separate into a fraction with a higher volume fraction of the continuous phase and a fraction with a lower volume fraction of the continuous

phase. Within this specification this phenomenon is referred to as segregation. Segregation can occur by the action of various forces, for instance centrifugal forces or gravity. Sedimentation is a form of segregation where the dispersed phase settles by gravity.

- 5 When a sediment is formed, part of the flow region within a reactor is blocked by a stagnant solid, reducing the volume available for free flow. With constant mass flux, the suspension will have to move through a smaller area, resulting in higher velocities of the continuous phase. This results in even more segregation and a non-ideal residence time distribution of the dispersed phase in the reactor.

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The conversion of solid particles in a suspension may be performed continuously in traditional pipe reactors or cascade reactors, provided that the starting particles easily form a stable homogeneous suspension, e.g., a sol or a gel, and are of a more or less uniform particle size. Even then limitations in the Solids to Liquid Ratio (SLR) may occur due to the rheological behaviour of the homogeneous suspension. High energy input, e.g., high-shear mixing, may alleviate these difficulties if the suspensions exhibit shear-thinning behaviour.

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Unfortunately, readily available iron oxides, iron hydroxides, and iron
20 oxyhydroxides are not easily suspendable and/or do not form stable homogeneous suspensions at high solids to liquid ratios. This is due either to their large particle size (say > 0.1 micron) and/or to their chemical incompatibility with the liquid, making segregation of the particles from the liquid very likely. This means that the particles will show a tendency to form a sediment layer, resulting in an uncontrolled
25 and non-ideal residence time distribution in the reactor, thereby hindering the conversion. This situation may be further aggravated when dealing with starting particles of different sizes.

Contrary to the case of the stable homogeneous suspensions described above, where high shear can assist in homogenisation and reduction of the viscosity,

unstable suspensions tend to segregate even faster when a high energy input is added to the system. Therefore, good mixing throughout the whole reactor and avoiding any dead or non-mixing zones is preferred to avoid non-ideal residence time distributions and to promote efficient conversion of the starting particles.

- 5 Alternatively, expensive chemicals need to be added in order to stabilise and disperse the suspension and to prevent segregation.

It has now been found that, as a result of agitation, starting iron compounds selected from the group consisting of iron oxides, iron hydroxides, iron oxyhydroxides, and mixtures thereof can be converted continuously, even at high
10 Solids to Liquid Ratios (SLR), in one or a series of separate vessels without an unacceptable level of segregation. Using high Solids to Liquid Ratios enables the use of relatively compact equipment and offers low costs of operation and energy consumption.

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The invention relates to a process for the conversion of a starting iron compound selected from the group consisting of iron oxides, iron hydroxides, iron oxyhydroxides, and mixtures thereof into a product iron compound, the product iron compound having different physical, chemical, and/or structural properties
20 than the starting iron compound, which process comprises the steps of:

- a) dispersing the starting iron compound in a liquid thus forming a suspension, and
b) feeding the suspension continuously through one or more agitated conversion vessel(s), in which vessel(s) the starting iron compound is converted into the
25 product iron compound under hydrothermal conditions.

A further advantage of the present invention resides in the possibility of fine-tuning particular (aspects of) process steps. If more than one conversion vessel is used, particular properties of the product iron compound can be controlled and/or

amplified by adapting, preferably optimising, the process conditions in at least one of these vessels. Within the framework of the present invention, this technique or procedure is called "de-coupling." Hence, de-coupling means that in the series of conversion vessels the process conditions in one or more of the vessels differ from those in the other vessel or vessels.

This de-coupling of process stages can be used for, *inter alia*, effective control of the structure of the product iron compound. The advantage of de-coupling is not trivial: by de-coupling the various process steps it becomes possible for instance to optimise the mixing and handling of the solid-liquid suspension which can change in rheological behaviour during its conversion. Thus segregation, in the form of either sedimentation or separation of solids with different particle sizes, can be avoided even at high SLR.

Moreover, de-coupling allows for optimisation of the conditions of multi-stage processes. For instance, the temperature or pH can be changed in each step and 15 additional compounds, like seeds or additives, can be added in any of the steps.

Suitable starting and product iron compounds include goethite (FeOOH), akaganeite, bernalite, feroxyhyte, ferrihydrite, lepidocrocite, limonite, maghemite, magnetite, hematite and wustite. It is noted that if the starting and product iron compounds are chemically equal, they have to differ by their structural and/or physical properties. Examples of such properties are surface area, pore volume, pore size distribution, catalytic activity, etc.

Examples of conversions which can be performed using the process according to the invention are the conversion of goethite to hematite, the conversion of hematite
25 with a specific porosity and surface area into hematite with another, preferably higher, porosity and surface area.

In the continuous process according to the invention the suspension flows substantially upward through the vessel(s) and/or the mixer exerts mainly axial

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forces on the suspension, such that the whole reactor is well-mixed and dead zones are avoided. With these measures, segregation of the solid particles and the liquid can be further suppressed. Also, an inhomogeneous distribution in the suspension of smaller particles on the one hand and larger particles on the other is substantially avoided.

The process according to the present invention can be conducted using one or more, preferably a series of two to five, more preferably three to five separate and substantially vertical conversion vessel(s). The conversion vessel(s) each comprise(s) a dedicated means for agitating the suspension. Axial or coaxial mixers are preferred.

Figure 1 shows a schematic layout of a plant for carrying out the present invention. The said plant comprises a feed preparation vessel 1, to which the starting iron compound and optionally one or more additives are added and mixed with liquid to form a suspension.

Suitable liquids include water, alcohols such as methanol, ethanol, n-propanol, isopropanol, etc., and hydrocarbon liquids such as toluene, hexane, white spirits, gasoline, etc., with water being preferred.

Suitable additives include HNO_3 , MgO , MnO , H_2CO_3 , NH_4HCO_3 , K_2CO_3 , Cr_2O_3 , SiO_2 , V_2O_5 , and mixtures thereof. It is noted that, if more than one conversion vessel is used, the additive(s) can be added to any one of the vessels. Alternatively, a part of the total amount of additive can be added to one of the conversion vessels, whereas another part can be added to another conversion vessel.

Forced by way of a feed pump, the resulting suspension is led continuously through a duct 2 to an inlet of the first of one or more, but preferably three to five, conversion vessels. By way of example, Figure 1 displays four such vessels: 3A-

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3D. Each of the vessels 3A-3D is provided with an outlet near its top, which is connected by means of a duct to an inlet near or in the bottom of a subsequent vessel, thus connecting the vessels 3A-3D in series. Each of the conversion vessels 3A-3D further contains an axial mixer 5, for instance a double-helix impeller or an anchor stirrer combined with an EKATO-INTERMIG® (an impeller suitable for mixing slurries with low viscosity, of which the outer blades pump downward while the inner blades pump upward), with which the suspension is both mixed substantially vertically and transported upward and downward while avoiding any dead or non-mixed zones. The mixers 5 are driven by electromotors (not shown) mounted on top of the conversion vessels 3A-3D. Typically, the mixers 5 are rotated at speeds from 20 to 500 revolutions per minute (rpm).

The conversion of the starting iron compound is conducted as hydrothermal conditions. Hydrothermal conditions are defined as a temperature above the boiling point of the liquid and a pressure above atmospheric, preferably autogeneous pressure. Depending on the liquid, the pressure resulting from the said temperatures may range from 1 to several tens of bars.

In case water is used as the liquid, suitable temperatures range from 150° to 375°C, preferably 200°-350°C.

The pH can range from 0-14, preferably between 0.1 and 9. The pH can be adjusted by acids and bases, which can be added to each conversion vessel separately.

It is noted that, if more than one conversion vessel is used, the temperature and pH in each of these vessels can differ, if so desired.

After conversion, the suspension containing the product iron compound particles leaves the last conversion vessel, e.g., the fourth vessel 3D, and is led through a duct 7 to a cooler unit 8, where the product is cooled down to, say, below 100°C. A mill 9 may be used to grind the particles to an average particle size, e.g., roughly

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1 micron, after which the suspension is separated into a product fraction of, e.g., 90% and a corresponding seeds fraction (10%). The seeds fraction may be ground to particles having an average size of 0.3 to 0.5 micron in a further mill 10, which is connected to a seeds buffer tank 11, which in turn is connected to either the feed preparation vessel 1 or any one of the conversion vessels 3A-3D. By way of example, figure 1 displays its connection to the feed preparation vessel.

The Solids to Liquid Ratio (SLR) of the suspension is defined as the weight ratio of solids, including crystal water, to liquid in the suspension. The process according to the invention allows processing of suspensions having an SLR up to 1.33. The optimal SLR depends on the rheological behaviour of the suspension, e.g. the tendency to form a gel.

The average residence time in the vessel(s), i.e. all vessels together, is preferably between 10 and 180 minutes.

If desired, the product iron compound formed in the present process may be shaped to form shaped bodies. In that case, it is preferred to continuously feed the suspension containing the product iron compound from cooler unit 8 or mill 9 to a shaping apparatus. Suitable shaping methods include spray-drying, pelletising, extrusion (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the suspension used for shaping should be adapted to the specific shaping step to be conducted. It might be advisable to partially remove the liquid used in the suspension and/or to add an additional or another liquid and/or to change the pH of the precursor mixture to make the suspension gellable and thus suitable for shaping. Various additives commonly used in the different shaping methods, e.g. extrusion additives, may be added to the precursor mixture used for shaping.

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If desired, the product iron compound can be calcined. Calcination is preferably performed at temperatures in the range of 150 to 600°C, preferably 200 to 450°C, for 15 minutes to 5 hours, preferably 30 minutes to 3 hours.

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The so-obtained product iron compound can suitably be used as or in a catalyst for, e.g., Fisher-Tropsch synthesis, ammonia synthesis, déhydrogenation of ethylbenzene to styrene, etc.

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CLAIMS

1. Process for the conversion of a starting iron compound selected from the group consisting of iron oxides, iron hydroxides, iron oxyhydroxides, and mixtures thereof into a product iron compound, the product iron compound having different physical, chemical, and/or structural properties than the starting iron compound, which process comprises the steps of:
 - a) dispersing the starting iron compound in a liquid thus forming a suspension, and
 - b) feeding the suspension continuously through one or more agitated conversion vessel(s), in which vessel(s) the starting iron compound is converted into the product iron compound under hydrothermal conditions.
2. Process according to claim 1 wherein the liquid is water and the temperature in the conversion vessel(s) ranges from 150 to 375°C.
3. Process according to claim 1 or 2 wherein the starting iron compound is selected from the group consisting of goethite (FeOOH), akaganeite, bernalite, feroxyhyte, ferrihydrite, lepidocrocite, limonite, maghemite, magnetite, hematite, and wustite.
4. Process according to any one of the preceding claims wherein the product iron compound is selected from the group consisting of goethite (FeOOH), akaganeite, bernalite, feroxyhyte, ferrihydrite, lepidocrocite, limonite, maghemite, magnetite, hematite, and wustite.
5. Process according to any one of the preceding claims wherein the product iron compound has a higher porosity and/or surface area than the starting iron compound.

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6. Process according to any one of the preceding claims wherein the suspension in step b) is fed through a series of from two to five conversion vessels.
- 5 7. Process according to any one of the preceding claims wherein the suspension flows substantially upward through the conversion vessel(s).

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ABSTRACT

The invention relates to a continuous process for the hydrothermal conversion of iron oxides, iron hydroxides, iron oxyhydroxides, and mixtures thereof into an iron
5 compound with different physical, chemical, and/or structural properties.

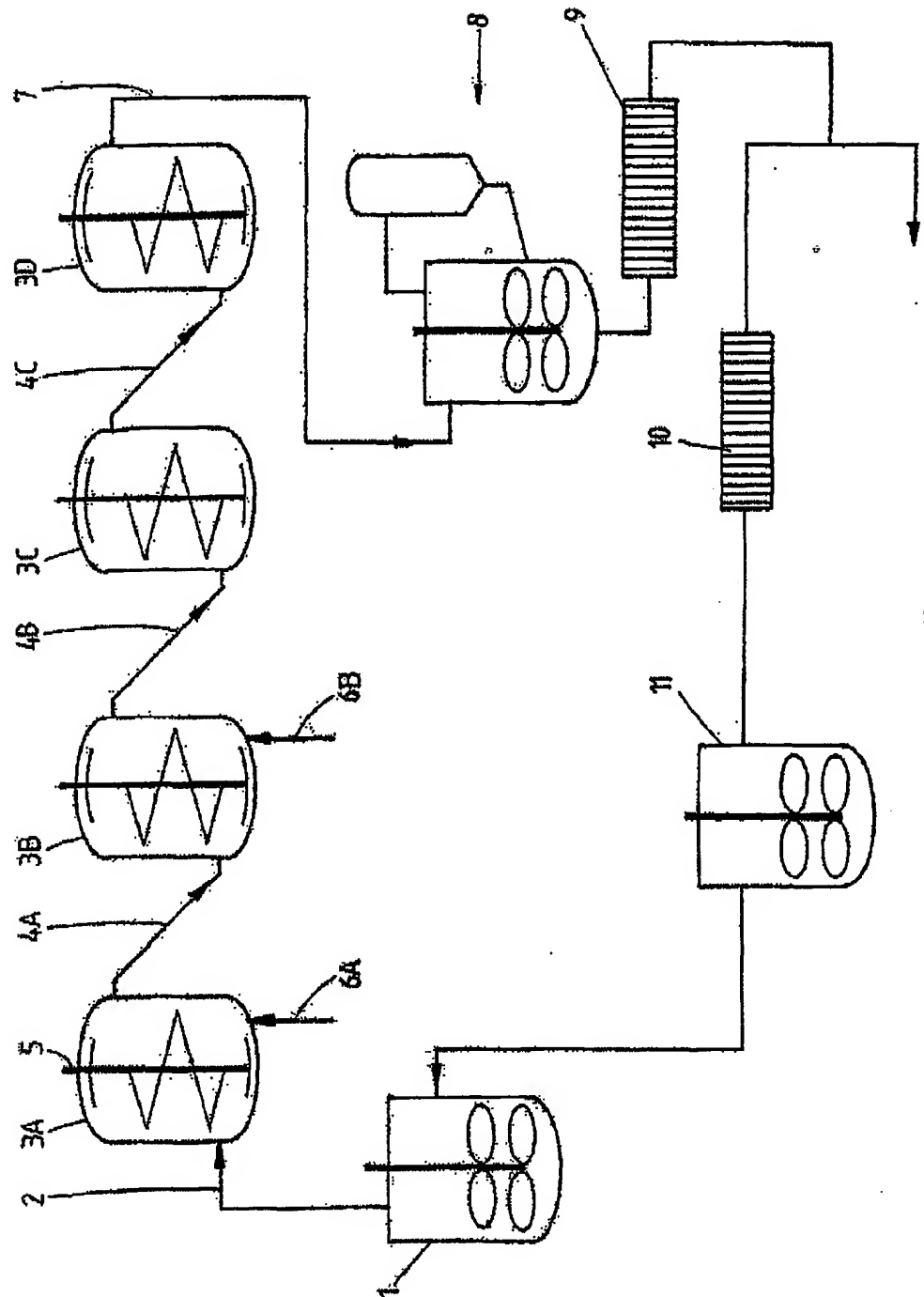
The process comprises the steps of

- a) dispersing the starting iron compound in a liquid thus forming a suspension,
and
- b) feeding the suspension continuously through one or more agitated conversion
10 vessel(s), in which vessel(s) the starting iron compound is converted into the
product iron compound under hydrothermal conditions.

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Figure 1



figure